

PROCESS FOR PRODUCTION OF SEMICONDUCTOR SUBSTRATE

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to a process for
producing a semiconductor substrate. More
specifically, the present invention relates to a
process for producing a monocrystalline semiconductor
on a dielectric-isolated or insulative material, or a
10 monocrystalline compound semiconductor on a
semiconductor substrate. Further the present invention
relates to a process for producing an electronic device
or an integrated circuit formed on a single crystalline
semiconductor layer.

15 Related Background Art

 The technique of formation of monocrystalline
Si (silicon) semiconductor on an insulative material is
well known as silicon-on-insulator (SOI) technique.
The device prepared by SOI technique has various
20 advantages which are not achievable by a bulk Si
substrate of usual Si integrated circuits as below:
1. Ease of dielectric isolation, and possibility of
high degree of integration,
2. High resistance against radioactive rays,
25 3. Low floating capacity, and possibility of high
speed operation,
4. Needlessness of the welling process,

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5. Preventability of latch-up,
6. Possibility of producing a complete depletion type field-effect transistor,
- and so forth.

5 The process of forming the SOI structure has been actively studied for several decades. The results of the studies are summarized, for example, in the paper: Special Issue; "Single-crystal silicon on non-single-crystal insulators"; edited by G.W. Cullen, 10 Journal of Crystal Growth; Vol.63, No.3, pp.429-590 (1983).

 SOS (silicon on sapphire) is known which is produced by heteroepitaxial growth of silicon on monocrystalline sapphire by CVD (chemical vapor 15 deposition). The SOS technique, which is successful as one of the SOI techniques, is limited in the application fields, because of many crystal defects caused by mismatch of the lattice at the interface between the Si layer and the underlying sapphire, 20 contamination of the Si layer with aluminum from the sapphire substrate, expensiveness of the substrate, and difficulty of large-area substrate formation.

 Recently, studies are being made to produce the SOI structure without using a sapphire substrate. The 25 studies are classified roughly into the two processes below:

1. A first process including surface oxidation of a

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monocrystalline Si substrate, local exposure of the Si substrate by opening a window, and epitaxial growth of Si laterally from the exposed portion as the seed to form an Si layer on SiO₂. (Si layer deposition on SiO₂)

- 5 2. A second process including SiO₂ formation beneath a monocrystalline SiO₂ substrate, utilizing the SiO₂ substrate as the active layer. (No Si layer deposition)

The device formed on a compound semiconductor exhibits performances, such as high speed, and
10 luminescence, which are not achievable by Si. Such types of devices are formed by epitaxial growth on a compound semiconductor substrate such as GaAs. The compound semiconductor substrate, however, has disadvantages of high cost, low mechanical strength,
15 and difficulty in formation of a large-area wafer. Accordingly, heteroepitaxial growth of a compound semiconductor on an Si wafer is being studied to attain low cost, high mechanical strength, and ease of production of a large-area wafer.

- 20 The above known process of the item 1 (Si layer deposition on SiO₂) includes methods of direct lateral epitaxial growth of monocrystalline Si layer by CVD; deposition of amorphous Si and subsequent heat treatment to cause solid-phase lateral epitaxial
25 growth; melting recrystallization to grow monocrystalline layer on an SiO₂ by irradiation of amorphous or polycrystalline Si layer with focused

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energy beam such as electron beam and laser beam; and zone melting recrystallization in which a bar-shaped heater is moved to scan with a belt-like melt zone.

These methods respectively have advantages and disadvantages, involving problems in process controllability, productivity, product uniformity, and product quality, and are not industrialized yet. For example, the CVD method requires sacrificial oxidation, giving low crystallinity in the solid-phase growth.

The beam annealing method involves problems in processing time of focused beam scanning and in controllability of beam superposition and focusing. Of the above methods, the zone melting recrystallization is the most advanced method, and is employed in relatively large scale integrated circuits. This method, however, still causes crystal defects in sub-grain boundaries, not being successful in production of a minority carrier device.

The above known process of the item 2 in which the Si substrate is not utilized as the seed for epitaxial growth includes the four methods below:

1. An oxidation film is formed on a monocrystalline Si substrate which has V-shaped grooves on the surface formed by anisotropical etching; a polycrystalline Si layer is deposited in a thickness approximate to that of the Si substrate on the oxidation film; and the back face of the Si substrate

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is ground to form a monocrystalline Si region isolated dielectrically by surrounding with the V-shaped grooves. This method involves problems in controllability and productivity in deposition of polycrystalline Si in a thickness of as large as several hundred microns, and in removal of the monocrystalline Si substrate by grinding at the back face to leave an isolated active Si layer only.

2. An SiO_2 layer is formed by ion implantation into a monocrystalline Si substrate (SIMOX: Separation by ion implanted oxygen). This is the most highly advanced method in view of the matching with the Si process. This method, however, requires implantation of oxygen ions in an amount of as much as 10^{18} ions/cm², which takes a long time, resulting in low productivity and high wafer cost. Further, the product has many remaining crystal defects, and does not have satisfactory properties for industrial production of a minority carrier device.

3. An SOI structure is formed by oxidation of porous Si for dielectric isolation. In this method, an N-type Si layer is formed in an island-like pattern on a P-type monocrystalline Si substrate surface by proton ion implantation (Imai, et al.: J. Crystal Growth, Vol. 63, p. 547 (1983)) or by epitaxial growth and patterning, and subsequently only the P-type Si substrate is made porous by anodic oxidation in an HF

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solution to surround the island-patterned N-type Si, and the N-type Si island is dielectrically isolated by accelerated oxidation. In this method, the isolated Si regions are fixed prior to the device process, which may limit the freedom of device design disadvantageously.

4. Differently from the above conventional SOI formation, a method has recently come to be noticed in which a monocrystalline Si substrate is bonded to another thermally oxidized monocrystalline Si substrate by heat treatment or use of an adhesive to form an SOI structure. This method requires uniform thinness of the active layer for the device: namely, formation of a film of a micron thick or thinner from a monocrystalline substrate of several hundred micron thick. This thin film may be formed by either of the two methods below.

1. Thin film formation by grinding, and
2. Thin film formation by selective etching.

The grinding method of "1" does not give readily a uniform thin film. In particular, formation of a film of submicron thickness results in thickness variation of tens of percent. This irregularity is a serious problem. With a larger diameter of the wafer, the uniformity of the thickness is much more difficult to attain.

The etching method of "2" is regarded to be

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effective for uniform thin film formation. This method, however, involves the problems of insufficient selectivity of about 10^2 at the highest, inferior surface properties after etching, and low crystallinity of the SOI layer because of the employed ion implantation, epitaxial or heteroepitaxial growth on a high-concentration B-doped Si layer. (C. Harendt, et al.: J. Elect. Mater., Vol. 20, p. 267 (1991); H. Baumgart, et al.: Extended Abstract of ECS 1st International Symposium of Wafer Bonding, pp. 733- (1991); and C.E. Hunt: Extended Abstract of ECS 1st International Symposium of Wafer Bonding, pp. 696- (1991))

The semiconductor substrate which is prepared by lamination requires two wafers essentially, and the most part of the one of the wafers is discarded by grinding or etching, thereby wasting the resource. Therefore the SOI prepared by lamination involves many problems in controllability, uniformity, production cost, and so forth in conventional processes.

A thin Si layer deposited on a light-transmissive substrate typified by a glass plate becomes amorphous or polycrystalline owing to disorder of crystallinity of the substrate, not giving high performance of the device. Simple deposition of Si does not give desired quality of single crystal layer owing to the amorphous crystal structure of the

substrate.

5 The light-transmissive substrate is essential
for construction of a light-receiving element such as a
contact sensor, and projection type of liquid crystal
image-displaying apparatus. Additionally, a driving
element of high performance is necessary for higher
density, higher resolution, and higher precision of the
sensor and of the image elements of the display.
Consequently, the element provided on a light
10 transmissive substrate is also required to have
monocrystalline layer of high crystallinity.

15 Amorphous Si or polycrystalline Si will not
give a driving element having required sufficient
performance because of the many defects in the crystal
structure.

20 As mentioned above, a compound semiconductor
device requires essentially a compound semiconductor
substrate. The compound semiconductor substrate,
however, is expensive, and is not readily formed in a
larger size.

25 Epitaxial growth of a compound semiconductor
such as GaAs on an Si substrate gives a grown film of
poor crystallinity owing to the difference in the
lattice constants and the thermal expansion
coefficients, thereby the resulting grown film being
not suitable for use for a device.

Epitaxial growth of a compound semiconductor on

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porous Si is intended for mitigation of misfit of the lattices. However, the substrate has not sufficient stability and reliability owing to the low thermal stability and long-term deterioration of the porous Si.

5 In view of the above-mentioned problems, Takao Yonehara, one of the inventors of the present invention, disclosed formerly a novel process for preparing a semiconductor member in European Patent Publication No. 0469630A2. This process comprises the
10 steps of forming a member having a nonporous monocrystalline semiconductor region on a porous monocrystalline semiconductor region; bonding the surface of a member of which the surface is constituted of an insulating substance onto the surface of the
15 nonporous monocrystalline semiconductor region; and then removing the porous monocrystalline semiconductor region by etching. This process is satisfactory for solving the above-mentioned problems. Further improvement of the disclosed process for higher
20 productivity and lower production cost will contribute greatly to the industries concerned.

SUMMARY OF THE INVENTION

25 The present invention intends to improve further the process disclosed in the above European Patent for producing a semiconductor member.

 The present invention further intends to

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provide a process for producing economically a semiconductor substrate having a monocrystalline layer or a compound semiconductor monocrystalline layer having excellent crystallinity, large-area and uniform flat surface on a surface of a monocrystalline substrate, in which the substrate is removed to leave the active semiconductor layer to obtain a monocrystalline layer or a compound semiconductor monocrystalline layer formed on the surface and having few defects.

The present invention still further intends to provide a process for producing a semiconductor substrate on a transparent substrate (light-transmissive substrate) for obtaining a monocrystalline Si semiconductor layer or a monocrystalline compound semiconductor layer having crystallinity as high as that of a monocrystalline wafer with high productivity, high uniformity, high controllability, and low production cost.

The present invention still further intends to provide a process for producing a semiconductor substrate useful in place of expensive SOS or SIMOX in production of a large scale integrated circuit of SOI structure.

A first embodiment of the process for producing a semiconductor substrate of the present invention comprises steps of: forming a nonporous monocrystalline

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semiconductor layer on a porous layer of the first substrate having the porous layer; bonding the nonporous monocrystalline layer onto a second substrate; separating the bonded substrates at the porous layer; removing the porous layer on the second substrate; and removing the porous layer constituting the first substrate.

A second embodiment of the process for producing a semiconductor substrate of the present invention comprises steps of: forming a nonporous monocrystalline semiconductor layer on a porous layer of a first substrate having the porous layer; bonding the nonporous monocrystalline layer onto a second substrate with interposition of an insulative layer; separating the bonded substrates at the porous layer; removing the porous layer on the second substrate; and removing the porous layer constituting the first substrate.

In the present invention, the lamination-bonded substrates are separated at the porous layer, and the porous layer is removed from the second substrate having a nonporous monocrystalline semiconductor layer. Thereby, a semiconductor substrate is prepared which has nonporous monocrystalline semiconductor layer of high quality. Furthermore, the first substrate can be repeatedly used for producing the semiconductor substrate in the next production cycle by removing the

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remaining porous layer on the first substrate after the separation of the two substrate. Thereby, the semiconductor substrate can be produced with higher productivity and lower cost.

5 The present invention enables preparation of a monocrystalline layer of Si or the like, or a monocrystalline compound semiconductor layer having excellent crystallinity similar to monocrystalline wafers on a substrate including a light-transmissive
10 substrate with advantages in productivity, uniformity, controllability, an production cost.

 The present invention further enables production of a semiconductor substrate which can be a substitute for expensive SOS and SIMOX in production of
15 large scale integrated circuits of an SOI structure.

 According to the present invention, the combined substrates are separated at the porous layer or layers into two or more substrates, and the one or more separated substrates may be used as a
20 semiconductor substrate after removal of the remaining porous layer, and the other substrate may be used repeatedly in the next production cycle of a semiconductor substrate.

 Further, according to the present invention,
25 two semiconductor substrates can be produced simultaneously by forming porous layers and nonporous monocrystalline layers on the both faces of a

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substrate, bonding thereto two other substrates, and separating the substrates at the porous layer.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Figs. 1A to 1E are schematic drawings for explaining an example of the process of the present invention.

10 Figs. 2A to 2E are schematic drawings for explaining another example of the process of the present invention.

Figs. 3A to 3E are schematic drawings for explaining a still another example of the process of the present invention.

15 Figs. 4A to 4E are schematic drawings for explaining a further example of the process of the present invention.

Figs. 5A to 5E are schematic drawings for explaining a still further example of the process of the present invention.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process for producing a semiconductor substrate of the present invention is described by employing a silicon substrate as an example.

25 The mechanical strength of porous silicon is much lower than that of bulk silicon depending on the porosity thereof. For instance, porous silicon having

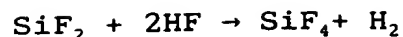
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a porosity of 50% is considered to have half a mechanical strength of bulk silicon. Therefore, on application of a tensile force, a compressive force, or a shearing force to a laminated wafer, the porous layer will be firstly broken. The larger the porosity of the porous layer, the less is the force for the breakdown of the layer.

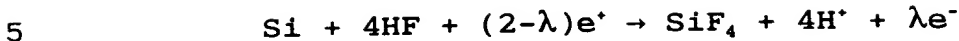
A silicon substrate can be made porous by anodization in an HF solution. The resulting porous Si layer has a density ranging from 1.1 to 0.6 g/cm³ depending on the HF solution concentration of from 50 to 20% in comparison with the density of 2.33 g/cm³ of monocrystalline Si. The porous layer is formed only on a P-type Si substrate, but is not formed on an N-type Si layer by the reasons described later. The porous Si layer has pores of about 600 Å in average diameter according to transmissive electron microscopy.

The porous Si was found by Uhler, et al. in the year 1956 during the study of electropolishing of semiconductors (A. Uhler: Bell Syst. Tech. J., vol. 35, p. 333 (1956)).

Unagami, et al. found that positive holes are required for anodization of Si in an HF solution, and the reactions proceed as shown in their report on dissolution of Si in anodization (T. Unagami, et al.: J. Electrochem. Soc., vol. 127, p. 476 (1980)) as below:



or



where e^+ and e^- represent respectively a positive hole and an electron; n and λ represent respectively the number of positive holes required for dissolving one Si atom. Unagami reported that porous Si is formed under the condition of $n > 2$, or $\lambda > 4$.

According to the above consideration, P-type Si which has positive holes can be made porous, whereas N-type Si cannot be made porous. This selectivity for porosity was evidenced by Nagano, et al., and Imai (Nagano, Nakajima, Yasuno, Oonaka, and Kajihara: Denshi Tsushin Gakkai Gijutsu Kenkyu Hokoku (Technical Research Report of Electronic Communication Society) vol. 79, SSD79-9549 (1979); and K. Imai: Solid-State Electronics, vol. 24, p. 159 (1981)).

On the other hand, a report is found that high concentration N-type Si can be made porous (R.P. Holmstrom and J.Y. Chi: Appl. Phys. Lett., vol. 42, p. 386 (1983)). Therefore, selection of the substrate is important for producing porous Si regardless of P-type or N-type.

The porous Si layer has pores of about 600 Å in

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average diameter by observation by transmission electron microscopy, and the density is less than half that of monocrystalline Si. Nevertheless, the single crystallinity is maintained, and thereon a

5 monocrystalline Si can be made to grow epitaxially in a layer. However, in the epitaxial growth at a temperature of 1000°C or higher, the internal pores will come to be rearranged, which impairs the accelerated etching characteristics. Therefore, low
10 temperature growth processes are preferred for epitaxial growth of the Si layer, such as molecular beam epitaxial growth, plasma CVD, reduced pressure CVD, photo-assisted CVD, bias sputtering, and liquid-phase epitaxial growth.

15 The porous layer has a large volume of voids therein, having a half or lower density of the material, and having a surface area remarkably large for the volume. Accordingly, the chemical etching is greatly accelerated in comparison with that of the
20 normal monocrystalline layer.

Embodiment 1

A first monocrystalline Si substrate 11 is made porous at the surface to form a porous layer 12 as shown in Fig. 1A. Then, nonporous monocrystalline Si
25 layer 13 is formed on the porous Si layer 12 as shown in Fig. 1B.

Another Si supporting substrate 14 is brought

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into contact with the nonporous monocrystalline Si layer 13 with interposition of an insulative layer 15 at room temperature as shown in Fig. 1C, and then the contacted matter was subjected to anode coupling, compression, heat treatment, or combination thereof to bond tightly the Si supporting substrate 14 and the monocrystalline layer 13 with interposition of the insulative layer 15. The insulative layer 15 may be formed preliminarily on either one of the monocrystalline Si layer 13 or the Si supporting substrate 14, or the three sheets may be bonded with an insulative thin film interposed.

Subsequently, the substrates are separated at the porous Si layer 12 as shown in Fig. 1D. On the Si supporting substrate 14, the layers have the structure of porous Si 12 / monocrystalline Si layer 13 / insulative layer 15 / Si supporting substrate 14.

The porous Si 12 is removed selectively by non-electrolytic wet chemical etching by use of at least one of a usual Si etching solution, hydrofluoric acid or a mixture of hydrofluoric acid with alcohol and/or hydrogen peroxide as the porous Si-selective etching solution, and buffered hydrofluoric acid or a mixture of hydrofluoric acid with alcohol and/or hydrogen peroxide to leave the thin-layered monocrystalline Si layer 13 on the insulative substrate 15+14. As described above in detail, the porous Si can be etched

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selectively by a usual Si etching solution owing to the extremely large surface area of the porous surface area.

Otherwise, the porous Si 12 is selectively
5 removed by grinding by utilizing the monocrystalline Si layer 13 as the grinding stopper.

Fig. 1E illustrates a semiconductor substrate of the present invention. The monocrystalline Si layer 13 is formed flat and uniformly in a thin layer on the
10 insulative substrate 15+14 over the entire large area of the wafer. The obtained semiconductor substrate is useful for production of insulation-isolated electronic elements.

The first monocrystalline Si substrate 11 may
15 be repeatedly used for the same use after removal of the remaining Si and surface flattening treatment if the surface has become roughened unacceptably in the next production cycle.

The method of separation of the two substrates
20 at the porous Si layer in the present invention includes crushing of the porous layer by compression on the both faces of the bonded substrates; pulling of the respective substrates in opposite directions; insertion of a jig or the like into the porous layer; application
25 of force in opposite directions parallel to the bonded face of the substrates; application of supersonic vibration to the porous layer; and so forth.

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The porosity of the porous Si layer suitable for the separation ranges generally from 10 to 80%, preferably from 20 to 60%.

Embodiment 2

5 A first monocrystalline Si substrate 21 is made porous at the surface to form a porous layer 22 as shown in Fig. 2A. Then a nonporous monocrystalline Si layer 23 is formed on the porous Si layer 22 as shown in Fig. 2B.

10 A light-transmissive supporting substrate 24 is brought into contact with the monocrystalline Si layer 23 with interposition of an insulative layer 25 at room temperature as shown in Fig. 2C, and then the contacted matter was subjected to anode coupling, compression,
15 heat treatment, or combination of the treatment to bond tightly the light-transmissive supporting substrate 24 and the monocrystalline layer 23 with interposition of the insulative layer 25. The insulative layer 25 may be formed preliminarily on either one of the
20 monocrystalline Si layer or the light-transmissive supporting substrate 24, or the three sheets may be bonded with interposition of an insulative thin film.

 Subsequently, the substrates are separated at the porous Si layer 22 as shown in Fig. 2D. On the
25 light-transmissive supporting substrate, the layers have the structure of porous Si 22 / monocrystalline Si layer 23 / insulative layer 25 / light-transmissive

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supporting substrate 24.

5 The porous Si 22 is removed selectively by non-electrolytic wet chemical etching by use of at least one of a usual Si etching solution, hydrofluoric acid or a mixture of hydrofluoric acid with alcohol and/or hydrogen peroxide as the porous Si-selective etching solution, and buffered hydrofluoric acid or a mixture of hydrofluoric acid with alcohol and/or hydrogen peroxide to leave a thin-layered monocrystalline Si
10 layer 23 on the insulative substrate 25+24. As described above in detail, the porous Si can be etched selectively by a usual Si etching solution because of the extremely large surface area of the porous surface area.

15 Otherwise, the porous Si 23 is selectively removed by grinding by utilizing the monocrystalline Si layer 22 as the grinding stopper.

Fig. 2E illustrates a semiconductor substrate of the present invention. The monocrystalline Si layer
20 23 is formed flat and uniformly in a thin layer on the insulative substrate 25+24 over the entire large area of the wafer. The obtained semiconductor substrate is useful for production of insulation-isolated electronic elements.

25 The presence of the interposed insulative layer 25 is not essential.

The first monocrystalline Si substrate 21 may

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be repeatedly used for the same use after removal of the remaining Si and surface flattening treatment if the surface has become roughened unacceptably in the next production cycle.

5 Embodiment 3

 A first monocrystalline Si substrate 31 is made porous at the surface to form a porous layer 32 as shown in Fig. 3A. Then a nonporous monocrystalline compound semiconductor layer 33 is formed on the porous Si layer 32 as shown in Fig. 3B.

 Another Si supporting substrate 34 is brought into close contact with the monocrystalline compound semiconductor layer 33 with interposition of an insulative layer 35 at room temperature as shown in Fig. 3C, and then the contacted matter was subjected to anode coupling, compression, or heat treatment, or combination of the treatments to bond tightly the Si supporting substrate 34 and the monocrystalline layer 33 with interposition of the insulative layer 35. The insulative layer 35 may be formed preliminarily on either one of the monocrystalline compound semiconductor layer or the Si supporting substrate 34, or the three sheets may be bonded with interposition of an insulative thin film.

 Subsequently, the substrates are separated at the porous Si layer 32 as shown in Fig. 3D. On the Si supporting substrate, the layers have the structure of

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porous Si 32 / monocrystalline compound semiconductor layer 33 / insulative layer 35 / Si supporting substrate 34.

5 The porous Si 32 is removed selectively by chemical etching by use of an etching solution which is capable of etching Si at a higher etching rate than the compound semiconductor to leave the thin-layered monocrystalline compound semiconductor layer 33 on the insulative substrate 35+34.

10 Otherwise, the porous Si 32 is selectively removed by grinding by utilizing the monocrystalline compound semiconductor layer 32 as the grinding stopper.

15 Fig. 3E illustrates a semiconductor substrate of the present invention. The monocrystalline compound semiconductor layer 33 is formed flat and uniformly in a thin layer on the insulative substrate 35+34 over the entire large area of the wafer. The obtained semiconductor substrate is useful as a compound
20 semiconductor substrate and for production of insulation-isolated electronic elements.

 When the substrate is used as a compound semiconductor substrate, the insulative layer 35 is not essential.

25 The first monocrystalline Si substrate 31 may be repeatedly used for the same use after removal of the remaining Si and surface flattening treatment if

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the surface has become roughened unacceptably in the next production cycle.

Embodiment 4

5 A first monocrystalline Si substrate 41 is made porous at the surface to form a porous layer 42 as shown in Fig. 4A. Then a nonporous monocrystalline compound semiconductor layer 43 is formed on the porous Si layer 42 as shown in Fig. 4B.

10 A light-transmissive supporting substrate 44 is brought into close contact with the monocrystalline compound semiconductor layer 43 with interposition of an insulative layer 45 at room temperature as shown in Fig. 4C, and then the contacted matter was subjected to anode coupling, compression, heat treatment, or
15 combination of the treatments to bond tightly the light-transmissive supporting substrate 44 with the monocrystalline layer 43 with interposition of the insulative layer 45. The insulative layer 45 may be formed preliminarily on either one of the
20 monocrystalline compound semiconductor layer or the light-transmissive supporting substrate 44, or the three sheets may be bonded with interposition of an insulative thin film.

25 Subsequently, the substrates are separated at the porous Si layer 42 as shown in Fig. 4D. On the light-transmissive supporting substrate, the layers have the structure of porous Si 42 / monocrystalline

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compound semiconductor layer 43 / insulative layer 45 /
light-transmissive supporting substrate 44.

5 The porous Si 42 is removed selectively by
chemical etching by use of an etching solution which is
capable of etching Si at a higher etching rate than the
compound semiconductor to leave a thin-layered
monocrystalline compound semiconductor layer 43 on the
insulative substrate 45+44.

10 Otherwise, the porous Si 42 is selectively
removed by grinding by utilizing the monocrystalline
compound semiconductor layer 42 as the grinding
stopper.

15 Fig. 4E illustrates a semiconductor substrate
of the present invention. The monocrystalline compound
semiconductor layer 43 is formed flat and uniformly in
a thin layer on the insulative substrate 45+44 over the
entire large area of the wafer. The obtained
semiconductor substrate is useful for production of
insulation-isolated electronic elements.

20 The insulative layer 45 is not essential in
this embodiment.

25 The first monocrystalline Si substrate 41 may
be repeatedly used for the same use after removal of
the remaining Si and surface flattening treatment if
the surface has become roughened unacceptably in the
next production cycle.

Embodiment 5

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5 A first monocrystalline Si substrate 51 is made porous at the both faces to form porous layers 52, 53 as shown in Fig. 5A. Then, nonporous monocrystalline compound semiconductor layers 54, 55 are formed on the porous Si layers 52, 53 as shown in Fig. 5B.

10 Two supporting substrates 56, 57 are brought into close contact with the monocrystalline semiconductor layers 54, 55 with interposition of insulative layers 58, 59 respectively at room temperature as shown in Fig. 5C, and then the contacted matter is subjected to anode coupling, compression, heat treatment, or combination of the treatments to bond tightly the supporting substrates 56, 57 and the monocrystalline layers 54, 55 with interposition of the
15 insulative layers 58, 59. In the bonding, the respective insulative layers 58, 59 may be formed preliminarily on either one of the monocrystalline semiconductor layer 54, 55 or the supporting substrate 56, or the five sheets may be bonded with interposition
20 of insulative thin films.

Subsequently, the substrates are separated into three at the both porous Si layers 52, 53 as shown in Fig. 5D. The two supporting substrates come to have a structure of porous Si / monocrystalline semiconductor
25 layer / insulative layer / supporting substrate (52/54/58/56, and 53/55/59/57).

The porous Si layers 52, 53 are removed .

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selectively by chemical etching to leave thin-layered monocrystalline semiconductor layers 54, 55 on the supporting substrates 58/56 and 59/57.

Otherwise, the porous Si 52, 53 is selectively removed by grinding by utilizing the monocrystalline semiconductor layers 54, 55 as the grinding stopper.

Fig. 5E illustrates semiconductor substrates prepared according to the present invention. The monocrystalline compound semiconductor layers are formed flat and uniformly in a thin layer on the supporting substrates over the entire large area of the two wafers at a time with a large area. The obtained semiconductor substrate is useful for production of insulation-isolated electronic elements.

The insulative intervening layers 58, 59 are not essential.

The supporting substrates 56, 57 need not be the same.

The first monocrystalline Si substrate 51 may be repeatedly used for the same use after removal of the remaining Si and surface flattening treatment if the surface has become roughened unacceptably in the next production cycle.

Example 1

A first monocrystalline (100) Si substrate of P-type having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was

anodized in an HF solution under the anodization conditions as below:

Current density: $5 \text{ mA} \cdot \text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
5 Time: 12 minutes
Thickness of porous Si: $10 \text{ } \mu\text{m}$
Porosity: 15 %

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall
10 of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a thickness of $1 \text{ } \mu\text{m}$ by CVD (chemical vapor deposition) under the growth conditions below:

15 Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate: $0.5/180 \text{ } \ell/\text{min}$
Gas pressure: 80 Torr
Temperature: 950°C
Growth rate: $0.3 \text{ } \mu\text{m}/\text{min}$

20 The face of the epitaxially grown Si layer was thermally oxidized to form an SiO_2 layer of 100 nm thick.

On the face of this Si substrate, a separately prepared second Si substrate having an SiO_2 layer of 500
25 nm thick was superposed with the SiO_2 layer inside, and the superposed matter was heat-treated at 900°C for 2 hours to bond the substrates tightly.

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A pulling force was applied to the resulting bonded wafer in the direction perpendicular to the wafer face in such a manner that a plate was bonded respectively to each of the both faces of the wafer with an adhesive and the plates were pulled to opposite directions with a jig. Consequently, the porous Si layer was broken to cause separation of the wafer into two sheets with the porous Si layers exposed.

The porous Si layer on the second substrate was etched selectively in a mixture of 49% hydrofluoric acid and 30% hydrogen peroxide (1:5) with agitation. The porous Si was etched and removed completely with the monocrystalline Si remaining unetched as an etching stopper. The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being 10^5 or higher. Therefore, thickness decrease of the nonporous layer by etching was practicably negligible (several ten Å).

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm on an Si oxide film. The monocrystalline Si layer did not change at all by the selective etching of the porous Si layer.

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was

retained.

Thus an SOI substrate was obtained which has a semiconductor layer of high quality.

5 The other Si substrate having been separated at the porous Si layer portion was etched in the same manner as above to remove the remaining porous layer, and its surface was polished. The obtained Si substrate was used repeatedly for the same use in the next production cycle. Thereby a plurality of SOI
10 substrates having a semiconductor layer of high quality were obtained.

Example 2

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15 A first monocrystalline (100) Si substrate of P-type having a diameter of 4 inches, a thickness of 525 μm , and a specific resistance of $0.01 \Omega \cdot \text{cm}$ was anodized in an HF solution under the anodization conditions as below:

Current density: $7 \text{ mA} \cdot \text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
20 Time: 12 minutes
Thickness of porous Si: $10 \mu\text{m}$
Porosity: 15 %

This substrate was oxidized at 400°C in an oxygen atmosphere for 2 hours. Thereby the inner wall
25 of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a

thickness of 0.5 μm by MBE (molecular beam epitaxy)
under the growth conditions below:

Temperature: 700°C
Pressure: 1×10^{-9} Torr
Growth rate: 0.1 nm/sec
Temperature: 950°C
Growth rate: 0.3 $\mu\text{m}/\text{min}$

The face of the epitaxially grown Si layer was
thermally oxidized to form an SiO_2 layer of 100 nm
thick.

On the face of the SiO_2 layer, was superposed a
separately prepared fused quartz substrate, and the
superposed matter was heat-treated at 400°C for 2 hours
to bond the substrates.

A sufficient compression force was applied
uniformly to the resulting bonded wafer in the
direction perpendicular to the wafer face such that
plates were bonded to each of the both faces of the
wafer with an adhesive and the compression force was
applied with the same jig as in Example 1.

Consequently, the porous Si layer was broken to
cause separation of the wafer into two sheets with the
porous Si layers exposed.

The porous Si layers were etched selectively in
a mixture of buffered hydrofluoric acid and 30%
hydrogen peroxide (1:5) with agitation. Thereby the
porous Si was etched and removed completely with the

monocrystalline Si remaining unetched as an etch-stop material. The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being, 10^5 or higher. Therefore, thickness decrease of the nonporous layer by etching was practicably negligible (several ten Å).

Consequently, a monocrystalline Si layer was formed in a thickness of $0.5\text{ }\mu\text{m}$ on a fused quartz substrate. The monocrystalline Si layer did not change at all by the selective etching of the porous Si layer.

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

A plurality of SOI substrates having a semiconductor layer of high quality were prepared by repeating the above process in the same manner as in Example 1.

Example 3

A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 6 inches, a thickness of $625\text{ }\mu\text{m}$, and a specific resistance of $0.01\text{ }\Omega\cdot\text{cm}$ was anodized in an HF solution under the anodization conditions as below:

Current density: $7\text{ mA}\cdot\text{cm}^{-2}$

Anodization solution: HF:H₂O:C₂H₅OH = 1:1:1

Time: 12 minutes

Thickness of porous Si: 10 μ m

Porosity: 15 %

5 This substrate was oxidized at 400°C in an
oxygen atmosphere for one hour. Thereby the inner wall
of the pores of the porous Si was covered with a
thermal oxidation film. On the porous Si,
monocrystalline GaAs was allowed to grow epitaxially in
10 a thickness of 1 μ m by MOCVD (metal organic chemical
vapor deposition) under the growth conditions below:

Source gas: TMG / AsH₃ / H₂

Gas pressure: 80 Torr

Temperature: 700°C

15 On the face of the formed GaAs layer, was
superposed a separately prepared second Si substrate,
and the superposed matter was heat-treated at 900°C for
one hour to bond the substrates tightly.

20 A sufficient compression force was applied to
the resulting bonded wafer in the same manner as in
Example 2. Thereby, the porous Si layer was broken to
allow the wafer to separate into two sheets with the
porous Si layers exposed.

25 Then, the oxide film on the inner wall of the
porous Si layer was removed by hydrofluoric acid, and
the porous Si was etched with a mixture of ethylene
diamine, pyrocatechol, and water (17 ml : 3 g : 8 ml)

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at 110°C. Thereby the porous Si was etched selectively and removed off completely with the monocrystalline GaAs remaining unetched as an etch-stopping material. The etching rate of the nonporous monocrystalline GaAs was extremely low and practicably negligible.

Consequently, a monocrystalline GaAs layer was formed in a thickness of 1 μm on an Si substrate. The monocrystalline GaAs layer did not change at all by the selective etching of the porous Si layer.

The cross-section of the GaAs layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the GaAs layer and the excellent crystallinity was retained.

A plurality of semiconductor substrates having a GaAs layer of high quality were prepared by repeating the above process in the same manner as in Example 2.

GaAs on an insulative film was also prepared by employing an Si substrate having an oxide film as the supporting substrate.

Example 4

A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 5 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in an HF solution under the anodization conditions as below:

Current density: 10 $\text{mA}\cdot\text{cm}^{-2}$

Anodization solution: HF:H₂O:C₂H₅OH = 1:1:1

Time: 24 minutes

Thickness of porous Si: 20 μm

Porosity: 17 %

5 This substrate was oxidized at 400°C in an
oxygen atmosphere for 2 hours. Thereby the inner wall
of the pores of the porous Si was covered with a
thermal oxidation film. On the porous Si,
monocrystalline AlGaAs was allowed to grow epitaxially
10 in a thickness of 0.5 μm by MBE (molecular beam
epitaxy).

On the face of the formed AlGaAs layer, was
superposed a face of a separately prepared low-melting
glass substrate. The superposed matter was heat-
15 treated at 500°C for 2 hours to bond the substrates
tightly.

A sufficient compression force was applied to
the resulting bonded wafer in the same manner as in
Example 2. Thereby, the porous Si layer was broken to
20 allow the wafer to separate into two sheets with the
porous Si layers exposed.

The porous Si was etched with hydrofluoric acid
solution. Thereby the porous Si was etched selectively
and removed off completely with the monocrystalline
25 AlGaAs remaining unetched as an etch-stopping material.
The etching rate of the nonporous monocrystalline
AlGaAs was extremely low and practicably negligible.

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Consequently, a monocrystalline AlGaAs layer was formed in a thickness of 0.5 μm on a glass substrate. The monocrystalline AlGaAs layer did not change at all by the selective etching of the porous Si layer.

The cross-section of the AlGaAs layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the AlGaAs layer and the excellent crystallinity was retained.

A plurality of semiconductor substrates having a GaAs layer of high quality were prepared by repeating the above process in the same manner as in Example 2.

Example 5

A first monocrystalline (100) Si substrate of P-type or N-type having been polished on the both faces and having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized on the both faces in an HF solution under the anodization conditions below:

Current density:	5 $\text{mA}\cdot\text{cm}^{-2}$
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:1:1
Time:	12 x 2 minutes
Thickness of porous Si:	10 μm each
Porosity:	15 %

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall

of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on the both faces of the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of 1 μm respectively by CVD (chemical vapor deposition) under the growth conditions below:

Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate: 0.5/180 ℓ/min
Gas pressure: 80 Torr
Temperature: 950°C
Growth rate: 0.3 $\mu\text{m}/\text{min}$

The faces of the formed epitaxial Si layers were thermally oxidized to form SiO_2 layers in a thickness of 100 nm.

On each of the faces of the SiO_2 layers, a separately prepared Si substrate having a 500-nm thick SiO_2 layer was superposed respectively with the SiO_2 layers inside, and the superposed matter was heat-treated at 600°C for 2 hours to bond the substrates tightly.

A sufficient pulling force was applied to the resulting bonded wafer in the direction perpendicular to the bonded wafer face in the same manner as in Example 1. Thereby, the two porous Si layers were broken to allow the wafer to separate into three sheets with the porous Si layers exposed.

The porous Si layers were etched selectively

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with a mixture of 49% hydrofluoric acid with 30% hydrogen peroxide (1:5) with agitation. Thereby the porous Si was etched selectively and removed completely with the monocrystalline Si remaining unetched as an etch-stopping material. The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being 10^5 or higher. Therefore, thickness decrease of the nonporous layer by etching was practicably negligible (several ten Å).

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm respectively on the two Si oxide films simultaneously. The monocrystalline Si layers did not change at all by the selective etching of the porous Si layer.

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

A plurality of semiconductor substrates having a semiconductor layer of high quality were prepared by repeating the above process in the same manner as in Example 1.

Example 6

A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 5 inches, a

thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in an HF solution under the anodization conditions below:

Current density: 7 $\text{mA}\cdot\text{cm}^{-2}$
5 Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time: 4 minutes
Thickness of porous Si: 3 μm
Porosity: 15 %

The anodization was conducted further under the conditions below:

Current density: 30 $\text{mA}\cdot\text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:3:2$
Time: 3 minutes
Thickness of porous Si: 10 μm
15 Porosity: 45 %

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of 0.3 μm by CVD under the conditions below:

Source gas: SiH_4
Carrier gas: H_2
25 Temperature: 850°C
Pressure: 1×10^{-2} Torr
Growth rate: 3.3 nm/sec

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The surface of the formed epitaxial Si layer was thermally oxidized to form SiO₂ layer in a thickness of 100 nm.

On the face of the SiO₂ layer, a separately prepared second Si substrate having a 500-nm thick SiO₂ layer was superposed with the SiO₂ layer inside, and the superposed matter was heat-treated at 700°C for 2 hours to bond the substrates tightly.

A sufficient pulling force was applied to the resulting bonded wafer in the direction perpendicular to the bonded wafer face in the same manner as in Example 1. Thereby, the porous Si layer was broken to allow the wafer to separate into two sheets with the porous Si layers exposed.

The porous Si on the second Si substrate was etched selectively with an etching solution of HF/HNO₃/CH₃COOH type. Thereby the porous Si was etched selectively and removed completely. The etching rate of the nonporous monocrystalline Si was extremely low, so that the thickness decrease of the nonporous layer by etching was practicably negligible.

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm on the Si oxide film. The monocrystalline Si layers did not change at all by the selective etching of the porous Si layer.

The cross-section of the Si layer was observed by transmission electron microscopy, and it was

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confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

5 A plurality of semiconductor substrates having a semiconductor layer of high quality were prepared by repeating the above process in the same manner as in Example 1.

Example 7

10 A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in an HF solution under the anodization conditions below:

15 Current density: 5 $\text{mA}\cdot\text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time: 12 minutes
Thickness of porous Si: 10 μm
Porosity: 15 %

20 This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of 1 μm by CVD under the
25 growth conditions below:

Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate: 0.5/180 ℓ/min

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Gas pressure: 80 Torr
Temperature: 950°C
Growth rate: 0.3 $\mu\text{m}/\text{min}$

5 The surface of the formed epitaxial Si layer
was thermally oxidized to form SiO_2 layer in a thickness
of 100 nm.

10 On the face of the SiO_2 layer, a separately
prepared second Si substrate having a 500-nm thick SiO_2
layer was superposed with the SiO_2 layer inside, and the
superposed matter was heat-treated at 900°C for 2 hours
to bond the substrates tightly.

15 A sufficient pulling force was applied to the
resulting bonded wafer in the direction perpendicular
to the bonded wafer face in the same manner as in
Example 1. Thereby, the porous Si layer was broken to
allow the wafer to separate into two sheets with the
porous Si layers exposed.

20 The porous Si layer on the second substrate was
ground selectively by utilizing the monocrystalline
layer as the stopper. Thereby the porous Si was
removed selectively.

25 Consequently, a monocrystalline Si layer was
formed in a thickness of 1 μm on the Si oxide film.
The monocrystalline Si layers did not change at all by
the selective grinding of the porous Si layer.

The cross-section of the Si layer was observed
by transmission electron microscopy, and it was

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confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

5 A plurality of semiconductor substrates having a semiconductor layer of high quality were prepared by repeating the above process in the same manner as in Example 1.

Example 8

10 A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in an HF solution under the anodization conditions below:

15 Current density: 5 $\text{mA}\cdot\text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time: 12 minutes
Thickness of porous Si: 10 μm
Porosity: 15 %

20 This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of 1 μm by CVD under the
25 conditions below:

Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate: 0.5/180 ℓ/min

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Gas pressure: 80 Torr
Temperature: 950°C
Growth rate: 0.3 $\mu\text{m}/\text{min}$

The surface of the formed epitaxial Si layer
5 was thermally oxidized to form SiO_2 layer in a thickness
of 100 nm.

On the face of the SiO_2 layer, a separately
prepared second Si substrate having a 500-nm thick SiO_2
layer was superposed with the SiO_2 layer inside, and the
10 superposed matter was heat-treated at 900°C for 2 hours
to bond the substrates tightly.

A supersonic energy was applied to the
resulting bonded wafer in a vessel provided with a
supersonic oscillator. Thereby, the porous Si layer
15 was broken to allow the wafer to separate into two
sheets with the porous Si layers exposed.

The porous Si layer on the second Si substrate
was etched selectively with a mixture of 49%
hydrofluoric acid with 30% hydrogen peroxide (1:5) with
20 agitation. Thereby the porous Si was etched
selectively and removed completely with the
monocrystalline Si remaining unetched as an etch-
stopping material. The etching rate of the nonporous
monocrystalline Si was extremely low, the selection
25 ratio of the etching rate of the porous Si being 10^5 or
higher. Therefore, thickness decrease of the nonporous
layer by etching was practicably negligible (several

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ten Å).

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm on the Si oxide film. The monocrystalline Si layers did not change at all by the selective etching of the porous Si layer.

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the porous Si remaining thereon.

Example 9

A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 4 inches, a thickness of 525 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in an HF solution under the anodization conditions as below:

Current density:	7 $\text{mA}\cdot\text{cm}^{-2}$
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:1:1
Time:	12 minutes
Thickness of porous Si:	10 μm
Porosity:	15 %

This substrate was oxidized at 400°C in an oxygen atmosphere for 2 hours. Thereby the inner wall of the pores of the porous Si was covered with a

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5	Temperature:	700°C
	Pressure:	1×10^{-9} Torr
	Growth rate:	0.1 nm/sec
	Temperature:	950°C
	Growth rate:	0.3 $\mu\text{m}/\text{min}$

On the face of the SiO_2 layer, was superposed a separately prepared fused quartz substrate, and the superposed matter was heat-treated at 400°C for 2 hours to bond the substrates.

The porous Si layer on the fused quartz substrate was etched selectively in a mixture of buffered hydrofluoric acid and 30% hydrogen peroxide (1:5) with agitation. Thereby the porous Si was etched and removed completely with the monocrystalline Si

remaining unetched as an etch-stopping material. The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being, 10^5 or higher. Therefore, thickness decrease of the nonporous layer by etching was practicably negligible (several ten Å).

Consequently, a monocrystalline Si layer was formed in a thickness of 0.5 μm on a fused quartz substrate. The monocrystalline Si layer did not change at all by the selective etching of the porous Si layer.

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

The same results were obtained without forming the oxide film of the surface of the epitaxial Si surface.

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the remaining porous Si and mirror-polishing of the surface.

Example 10

A first monocrystalline (100) Si substrate of P-type or N-type having a polished face on each side and having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized

on both sides in an HF solution under the anodization conditions below:

Current density: $5 \text{ mA} \cdot \text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
5 Time: 12×2 minutes
Thickness of porous Si: $10 \text{ } \mu\text{m}$ each
Porosity: 15 %

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall
10 of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on the both faces of the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of $1 \text{ } \mu\text{m}$ by CVD (chemical vapor deposition) under the conditions
15 below:

Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate: $0.5/180 \text{ l/min}$
Gas pressure: 80 Torr
Temperature: 950°C
20 Growth rate: $0.3 \text{ } \mu\text{m/min}$

The surfaces of the formed epitaxial Si layers were thermally oxidized to form SiO_2 layers in a thickness of 100 nm.

On each of the faces of the SiO_2 layers, a
25 separately prepared second Si substrate having a 500-nm thick SiO_2 layer was superposed with the SiO_2 layer inside, and the superposed matter was heat-treated at

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600°C for 2 hours to bond the substrates tightly.

5 The porous layers were bared at the edge face of the wafer, and a liquid such as water was allowed to penetrate into the porous Si. The entire bonded wafer was heated or cooled, whereby the porous Si layers were broken owing to expansion or other causes to allow the wafer to separate into three sheets with the porous Si layers exposed.

10 The porous Si layers were etched selectively with a mixture of 49% hydrofluoric acid with 30% hydrogen peroxide (1:5) with agitation. Thereby the porous Si was etched selectively and removed completely with the monocrystalline Si remaining unetched as an etch-stopping material. The etching rate of the
15 nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being 10^5 or higher. Therefore, thickness decrease of the nonporous layer by etching was practicably negligible (several ten Å).

20 Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm respectively on the two Si oxide films simultaneously. The monocrystalline Si layers did not change at all by the selective etching of the porous Si layer.

25 The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed

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in the Si layer and the excellent crystallinity was retained.

The same results were obtained without formation of the oxide film on the surface of the epitaxial Si layer.

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the remaining porous Si and flattening of the surface by hydrogen treatment.

10 Example 11

A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 5 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in an HF solution under the anodization conditions below:

Current density: $7 \text{ mA}\cdot\text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time: 4 minutes
Thickness of porous Si: 3 μm
20 Porosity: 15 %

The anodization was conducted further under the conditions below:

Current density: $30 \text{ mA}\cdot\text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:3:2$
25 Time: 3 minutes
Thickness of porous Si: 10 μm
Porosity: 45 %

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of 0.3 μm by CVD under the conditions below:

Source gas:	SiH_4
Carrier gas:	H_2
Temperature:	850°C
Pressure:	1×10^{-2} Torr
Growth rate:	3.3 nm/sec

The surface of the formed epitaxial Si layer was thermally oxidized to form SiO_2 layer in a thickness of 100 nm.

On the face of the SiO_2 layer, a separately prepared second Si substrate having a 500-nm thick SiO_2 layer was superposed with the SiO_2 layer inside, and the superposed matter was heat-treated at 700°C for 2 hours to bond the substrates tightly.

A force was applied to the first (or second) substrate in a direction parallel to the second (or first) substrate, whereby the porous Si layer was broken by the shear stress to allow the wafer to separate into two sheets with the porous Si layers exposed.

The porous Si layer was etched selectively with

an HF/HNO₃/CH₃COOH type etching solution. Thereby the porous Si was etched selectively and removed completely. The etching rate of the nonporous monocrystalline Si was extremely low, so that the thickness decrease of the nonporous layer by etching was practicably negligible.

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm on the Si oxide layer. The monocrystalline Si layer did not change at all by the selective etching of the porous Si layer.

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

The same results were obtained without forming the oxide film on the surface of the epitaxial Si layer surface.

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the remaining porous Si.

Example 12

A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 5 inches, a thickness of 625 μm, and a specific resistance of 0.01 Ω·cm was anodized in an HF solution under the anodization conditions below:

Current density: $7 \text{ mA} \cdot \text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time: 4 minutes
Thickness of porous Si: $3 \text{ } \mu\text{m}$
5 Porosity: 15 %

The anodization was conducted further under the conditions below:

Current density: $30 \text{ mA} \cdot \text{cm}^{-2}$
Anodization solution: $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:3:2$
10 Time: 3 minutes
Thickness of porous Si: $10 \text{ } \mu\text{m}$
Porosity: 45 %

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall
15 of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of $0.3 \text{ } \mu\text{m}$ by CVD under the conditions below:

20 Source gas: SiH_4
Carrier gas: H_2
Temperature: 850°C
Pressure: $1 \times 10^{-2} \text{ Torr}$
Growth rate: 3.3 nm/sec

25 The surface of the formed epitaxial Si layer was thermally oxidized to form SiO_2 layer in a thickness of 100 nm .

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The same results were obtained without forming the oxide film on the surface of the epitaxial Si layer

surface.

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the remaining porous Si.

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